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## Wairakite: A Potential Indicator of Fluid Mixing

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### Keywords

*Wairakite, Bulalo, Tiwi, Karaha-Telaga Bodas, calc-silicate minerals*

### ABSTRACT

Wairakite is a common geothermal mineral. Detailed paragenetic studies indicate that wairakite typically forms after the deposition of epidote  $\pm$  prehnite and later anhydrite + calcite. Epidote and prehnite are interpreted as products of early, high temperature alteration associated with upwelling reservoir fluids whereas calcite and anhydrite are related to descending acidic condensates. Calculated stability relationships among the calc silicate minerals indicates that cooling and/or decreasing pH will lead to the deposition of wairakite instead of epidote, whereas decreasing pH favors wairakite over prehnite. We infer, from the petrographic relationships, that these changes occur when descending condensate mixes with the in-situ reservoir fluids during the waning stages of geothermal activity. Fluid inclusion measurements indicate wairakite is commonly deposited between temperatures of ~235 and 300°C.

### Introduction

Wairakite is a calcium aluminum silicate ( $\text{CaAl}_2\text{Si}_4\text{O}_{12}(\text{H}_2\text{O})$ ) common in many active geothermal systems. It was first described from the geothermal field at Wairakei, New Zealand by Steiner (1955). Despite its widespread occurrence in geothermal fields, it is rarely reported from epithermal deposits that represent fossil geothermal systems. The reasons for this are not known. Compilations of mineral distributions by Henley and Ellis (1983) suggest that wairakite is typical of moderate temperature environments. They concluded that wairakite is stable from temperatures of 200° to ~310°C. At these temperatures, there is significant overlap between the thermal stability fields of wairakite, epidote and prehnite (Bird et al., 1984). Other calc-silicate minerals, which include the

clinopyroxenes, amphiboles and garnets, are typically only found where temperatures were greater than 300°C.

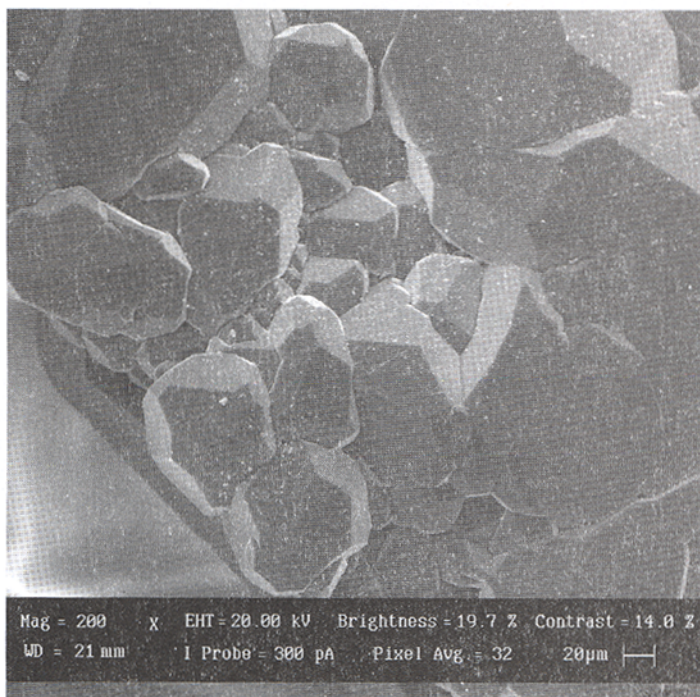
The relationships between wairakite, epidote and fluid chemistry were first discussed by Browne and Ellis (1970) to explain differences in the alteration assemblages at Wairakei and Broadlands-Ohaaki in New Zealand. At Wairakei, epidote and wairakite are present but calcite is rare whereas at Broadlands-Ohaaki, calcite is common but the calc silicates are not. The two geothermal fields have similar temperatures, reservoir lithologies and fluid salinities but different  $\text{CO}_2$  contents. Browne and Ellis (1970) concluded that the deposition of calc-silicate minerals at Wairakei was a result of the low  $\text{CO}_2$  contents of the reservoir fluid ( $\text{mCO}_2 = 0.01$ ), whereas the higher  $\text{CO}_2$  contents of Broadlands-Ohaaki ( $\text{mCO}_2 = 0.15$ ) favored the deposition of calcite. At this higher  $\text{CO}_2$  content, the deposition of epidote, represented thermodynamically by zoisite, was not expected, and while wairakite could precipitate, its stability field was greatly reduced. At 260°C and for  $\text{mCO}_2 = 1$ , the "calcite blind" is drawn across the stability fields of both epidote and wairakite, precluding their deposition, and only calcite is precipitated.

In this paper, we extend the work of Browne and Ellis (1970) and examine the deposition of wairakite in its broader paragenetic framework. Mineral relationships from three representative geothermal fields are presented and summarized in temperature-composition space. The results suggest that wairakite is commonly precipitated during the late stages of alteration in geothermal systems and that it can be a useful indicator of fluid mixing.

### General Features of Wairakite

Wairakite is a monoclinic mineral that commonly forms nearly equant multifaceted white crystals (Figure 1, overleaf). It has a distinct (100) cleavage and is moderately hard (5-5.6). In thin section, wairakite is colorless under plane polarized light. It exhibits weak birefringence and complex twinning under crossed nicols. These optical properties are distinctive and consequently, wairakite is unlikely to be misidentified.





**Figure 1.** Scanning electron microscope image of wairakite crystals from a depth of 1747.4 m in well K-33, Karaha-Telaga Bodas, Indonesia.

Although the crystals are often decorated with numerous fluid inclusions, they frequently leak when heated. As a result, fluid inclusion data obtained on wairakite must be interpreted with caution.

There is little compositional data on wairakite. Most analyses indicate its composition is close to stoichiometric.  $\text{Na}_2\text{O}$  is the most abundant contaminant, being present in concentrations up to 1.06 weight percent in wairakite from Wairakei. Minor concentrations of  $\text{K}_2\text{O}$ ,  $\text{Cs}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SrO}$  have also been reported but all are less than 0.2 weight percent (Steiner, 1955; Browne, 1977).

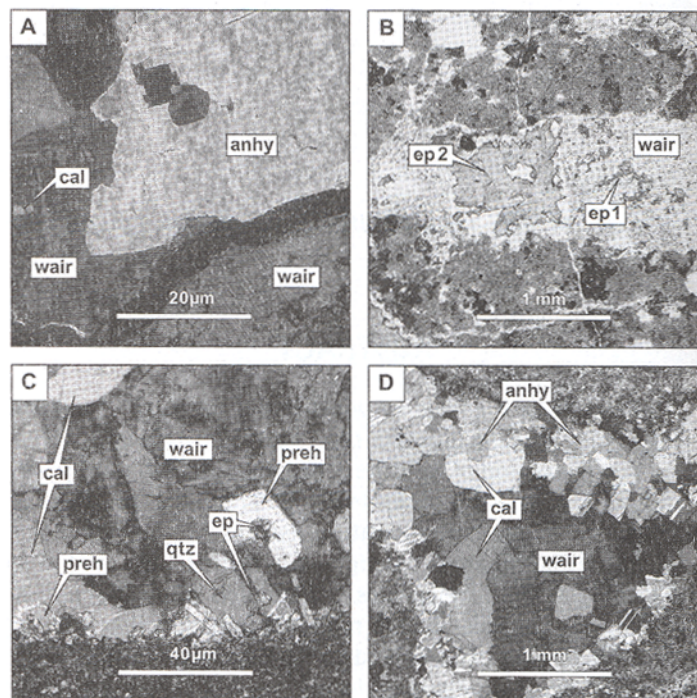
Wairakite has been found in both liquid- and vapor-dominated geothermal systems and in virtually all reservoir lithologies, including lava flows, pyroclastic and volcanoclastic deposits and silicic to basic intrusive rocks. In the following section, the occurrence of wairakite in the volcanic-hosted liquid-dominated geothermal systems at Tiwi and Bulalo in the Philippines and in the partially vapor-dominated geothermal system at Karaha-Telaga Bodas, Indonesia is described. These systems were chosen because mineral relationships are particularly well documented and because of the range of temperatures, fluid compositions and physical processes they exhibit.

## Paragenetic Relationships

### Bulalo, Philippines

Bulalo is a high-temperature geothermal system located on the island of Luzon, approximately 70 km southeast of Manila. The reservoir rocks consist of andesite lava flows and pyroclastic and volcanoclastic deposits (Golla et al., 2001). The mineral assemblages define a relatively simple paragenesis that

appears to represent a single cycle of heating and cooling (J. Layton unpub. data; 2003). Epidote is the common early high temperature mineral, although minor actinolite and garnet have been observed. Anhydrite and calcite formed late in the paragenetic sequence and represent the incursion of marginal waters. Although most of the wairakite is associated with anhydrite and calcite, the textural relationships indicate that the three minerals were not deposited contemporaneously (Figure 2A). In most samples, wairakite postdates the calcite and anhydrite; rarely later calcite and anhydrite are present. Wairakite formed earlier in the paragenesis is uncommon. In one sample, the textures indicate that deposition of wairakite alternated with epidote (Figure 2B).



**Figure 2.** Photomicrographs of wairakite-bearing assemblages. A) Wairakite after anhydrite. From 2705.4 m in well B-82 (Bulalo). B) Alternating episodes of epidote and wairakite. From 1270.2 m in well B-27 (Bulalo). The first generation of epidote (ep 1) is encapsulated in wairakite; the second (ep 2) forms large crystals in vugs in the wairakite. C) Calc-silicate minerals from 1658.1 m in well K-33 (Karaha-Telaga Bodas). The paragenesis from oldest to youngest is 1) epidote; 2) prehnite; 3) quartz; 4) calcite; and 5) wairakite. D) Wairakite after anhydrite and calcite. From 1546.9 m in well K-21 (Karaha-Telaga Bodas). Abbreviations: anhy = anhydrite; cal = calcite; ep = epidote; preh = prehnite; qtz = quartz; wair = wairakite.

Homogenization temperatures of primary fluid inclusions, which at these shallow depths approximate the true trapping temperatures, indicate deposition of epidote occurred at 298° to 310°C in well B-27-1. It can be argued, based on the observation that wairakite was deposited between periods of epidote deposition, that the wairakite in this sample was also deposited at a temperature close to 300°C. Primary fluid inclusions in calcite, which postdates wairakite in Bulalo 81-1 (2011.7-2014.7 m) provide a probable lower temperature limit for the deposition of wairakite. These inclusions yielded homogenization temperatures of 218° to 223°C.



## Tiwi, Philippines

Tiwi is located on the island of Luzon, approximately 300 km south of Manila. Detailed paragenetic and geologic studies were conducted on core from well Matalibong-25 (Moore et al, 2000a). The well encountered andesite and basaltic andesite flows, flow breccias and volcanoclastic rocks deposited in a subaerial environment and sandstones deposited in a subaqueous environment.

The overall sequence of secondary minerals is similar to that of Bulalo, although the data suggest several episodes of heating and incursion of marginal waters (Moore et al, 2000a). Epidote, adularia and quartz represent early high-temperature minerals. Wairakite was deposited late in the paragenesis where it is most often associated with anhydrite and calcite. Rarely, it is associated with sericite. Temperatures of wairakite deposition are not as well constrained as those at Bulalo, although the available fluid inclusion data suggest a similar temperature range. The upper limit of the homogenization temperatures in quartz and calcite are close to the boiling point for depth and reach a maximum of  $\sim 335^{\circ}\text{C}$  at  $\sim 2000$  m depth. These temperatures also represent an upper limit for wairakite deposition at Tiwi. The minimum fluid inclusion temperatures in calcite, anhydrite and quartz are  $\sim 235^{\circ}\text{C}$  and do not vary with depth. The consistent temperatures suggest the thermal regime remained stable for a period of time. These temperatures provide a lower limit for wairakite deposition.

## Karaha-Telaga Bodas, Indonesia

Karaha-Telaga Bodas is a young, partially vapor-dominated geothermal system located on the northern flank of Galunggung Volcano in western Java. Reservoir rocks consist of andesitic and basaltic lava flows and pyroclastic and volcanoclastic deposits. Mineral assemblages at Karaha-Telaga Bodas, like those at Bulalo, record a simple thermal history (Moore et al, 2000b). Early heating is represented by high temperature assemblages that vary with depth and include epidote, amphiboles, biotite, clinopyroxene, garnet, tourmaline and later prehnite. A distinctive assemblage of chalcedony and quartz marks the transition from heating to cooling and from a liquid to vapor-dominated regime. This assemblage was deposited when the reservoir fluids underwent decompression and boiling associated with the formation of Kawah Galunggung at 4200 years BP. Subsequent assemblages are dominated by anhydrite and calcite at shallow to intermediate depths and the addition of wairakite at intermediate to greater depths. Wairakite postdates prehnite and later anhydrite  $\pm$  calcite (Figure 2C, D). At a depth of 1637 m in well K-21, quartz formed during decompression coprecipitated first with epidote, which had been growing along the vein margins, then wairakite and finally calcite. Secondary fluid inclusions in quartz from 1628 m depth record a temperature of  $\sim 255^{\circ}\text{C}$  but extrapolation of fluid inclusion temperatures from shallower depths suggests temperatures could have been as high as  $\sim 300^{\circ}\text{C}$  at the time of quartz and wairakite deposition. The present-day downhole temperatures of the wells are similar to the minimum temperatures obtained on fluid inclusions

trapped in late-stage calcite and anhydrite. These data suggest that rock temperatures were never substantially lower than they are today and that the present-day values can be used to obtain a minimum temperature estimate of wairakite formation. These temperatures range from  $220^{\circ}$  to  $250^{\circ}\text{C}$ .

At Karaha-Telaga Bodas, prehnite formed after epidote but prior to wairakite. Petrographic relationships demonstrate that prehnite began to grow before quartz was deposited although the two minerals locally coprecipitated. Relationships between the calc-silicate minerals, quartz and calcite from well K-33 are shown in Figure 2C. In this well, prehnite is found to a depth of 1856.2 m. Fluid inclusions in quartz from the lower part of the prehnite zone (1848.6 m) record temperatures up to  $285^{\circ}\text{C}$ . These fluid inclusion temperatures provide a reasonable upper estimate for prehnite deposition in this well.

## Discussion

The mineral relationships from the three geothermal systems described show similar paragenetic sequences, despite differences in their time-temperature composition histories. In each case, epidote is among the earliest of the calc-silicate minerals to form. At both Karaha-Telaga Bodas and Bulalo, it is associated locally with garnet and actinolite. Fluid inclusions trapped in epidote frequently record temperatures in excess of  $300^{\circ}\text{C}$ . Prehnite represents the second stage in the paragenetic sequence. At Karaha-Telaga Bodas, prehnite has grown directly on epidote, without evidence of intervening mineral assemblages. Anhydrite and calcite represent the third stage in the paragenesis. These minerals frequently show evidence of dissolution. The fourth stage is represented by the deposition of wairakite. Later calcite and less commonly anhydrite may be present.

Although wairakite frequently encapsulates epidote, few examples of epidote-wairakite intergrowths suggesting "contemporaneous" deposition have been identified. Although clear evidence of alternating episodes of wairakite and epidote are observed at Bulalo, most of the wairakite, as elsewhere, formed late in the paragenetic sequence, after anhydrite and calcite.

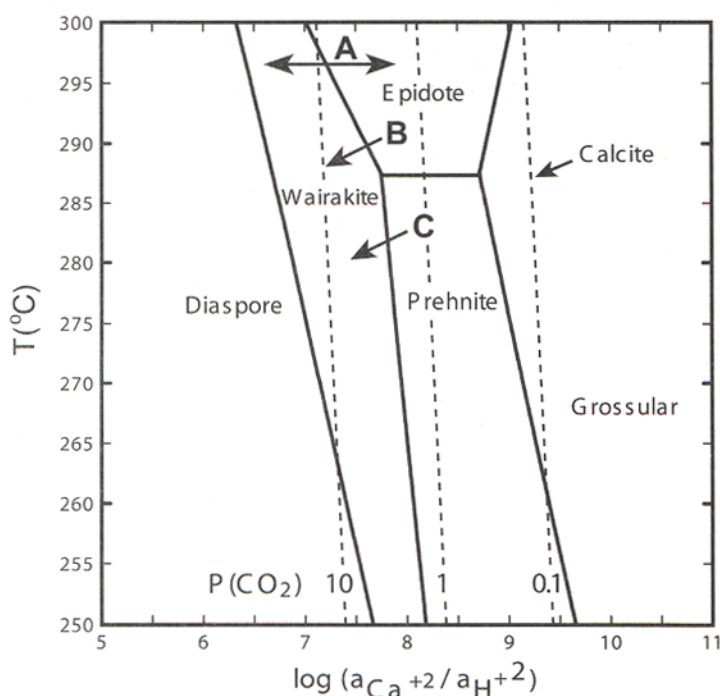
The fluid inclusion data, although not on inclusions trapped in wairakite, provide constraints on the temperatures of deposition. These data indicate that wairakite, in the fields studied, was deposited at temperatures between  $\sim 235^{\circ}$  and  $300^{\circ}\text{C}$ .

## Summary and Conclusions

The stability field of wairakite occupies a relatively narrow region in temperature-composition space (Figure 3, overleaf). At the temperature extremes defined by the fluid inclusion data, the stability field of wairakite is greatly reduced, diminishing the opportunity for its deposition. Increasing concentrations of  $\text{Fe}^{+3}$  in epidote will further diminish the stability field of wairakite while expanding the stability field of epidote.

The deposition of wairakite instead of epidote is favored by decreasing temperature and/or decreasing pH. Prehnite is favored over epidote by decreasing temperature, whereas wairakite is stabilized over prehnite by decreasing pH. Three





**Figure 3.** Mineral stability relations in the system Ca-Fe-Al-Si-H<sub>2</sub>O-Cl assuming equilibrium with quartz and pyrite, log(10) O<sub>2</sub>(g) fugacity in bars = -33, and log(10) activity H<sub>2</sub>S(aq) = -2.44. Conditions are representative of computed downhole conditions in well Matalibong-25, Tiwi, Philippines (Bruton et al., 1997). Dotted lines show calcite stability at various CO<sub>2</sub> pressures in bars. At P(CO<sub>2</sub>) = 10 bars, the epidote and most of the wairakite fields are covered by the "calcite blind". Quartz thermodynamic data from Fournier (1983); remaining data from Johnson and Lundeen (1997) with equilibrium constants of wairakite reduced by 0.6 log units to better represent commonly observed relations between wairakite and fluid chemistry in New Zealand geothermal systems (Bruton, unpub. ms.). See text for a discussion of the paths labeled A, B and C.

paths are schematically shown in Figure 3. Path A will result in alternating episodes of epidote and wairakite at constant temperature but changing fluid composition. This path describes the high temperature formation of these minerals at Bulalo. Path B shows the effects of decreasing pH and temperature to produce wairakite instead of epidote. Path C will lead to the formation of wairakite instead of prehnite. Although changes in pH could be produced by the influx of CO<sub>2</sub>, gas addition will not promote cooling or the deposition of the commonly associated anhydrite. Cooling and anhydrite deposition is most likely to occur when descending waters enriched in sulfate mix with an initially near-neutral pH reservoir fluid.

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## References

- Bird, D.K., Schiffman, P., Elders, W.A., Williams, A.E., and McDowell, S.D., 1984. "Calc-silicate mineralization in active geothermal systems: Economic Geology," v. 79, p. 671-695.
- Browne P.R.L., 1977. "Occurrence and hydrothermal alteration of diabase, Heber geothermal field, Imperial Valley, California." Institute of Geophysics and Planetary Sciences, University of California, Riverside, Rept. UCR/IGPP-77-9, 61 p.
- Browne, P.R.L. and Ellis, A.J., 1970. "The Ohaki-Broadlands hydrothermal area, New Zealand mineralogy and related chemistry." American Journal of Science, v.269, p. 97-131.
- Bruton, C.J., Moore, J.N., and Powell, T.S., 1997. "Geochemical analysis of fluid-mineral relations in the Tiwi Geothermal Field, Philippines." Proc. 22nd Workshop on Geothermal Reservoir Engineering, Stanford, CA, p. 457-463.
- Fournier, R.O., 1983. "A method of calculating quartz solubilities in aqueous sodium chloride solution." Geochimica et Cosmochimica Acta, v. 47, p. 579-586.
- Golla, G.U., Abrigo, F.V., Alarcon, B.O., Molling, P.A. and Stimac, J., 2001. "The Bulalo geothermal field, Philippines: conceptual model of a prolific geothermal system." Proceedings 22nd PNOC-EDC Geothermal Conference, p. 123-132.
- Henley, R.W. and Ellis A.J., 1983. "Geothermal systems ancient and modern: a geochemical review: Earth-Science Reviews," v. 19, p. 1-50.
- Johnson, J.W. and Lundeen, S.R., 1997. "GEMBOCHS thermodynamic data files for use with the EQ3/6 software package." Lawrence Livermore National Laboratory internal report.
- Moore, J. N., Powell, T. S., Heizler, M. T. and Norman, D. I., 2000a. "Mineralization and hydrothermal history of the Tiwi geothermal system, Philippines." Economic Geology, v. 95, p. 1001-1023.
- Moore, J., Lutz, S., Renner, J., McCulloch, J. and Petty, S., 2000b. "Evolution of a volcanic-hosted vapor-dominated system: petrologic and geochemical data from well T-8, Karaha-Telaga Bodas." Indonesia: GRC Transactions, v. 24, p. 259-263.
- Steiner A., 1955. "Wairakite, the calcium analogue of analcime, a new zeolite mineral." Mineralogical magazine, v. 30, p. 691-708.